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METHODS

of the Chemists of the

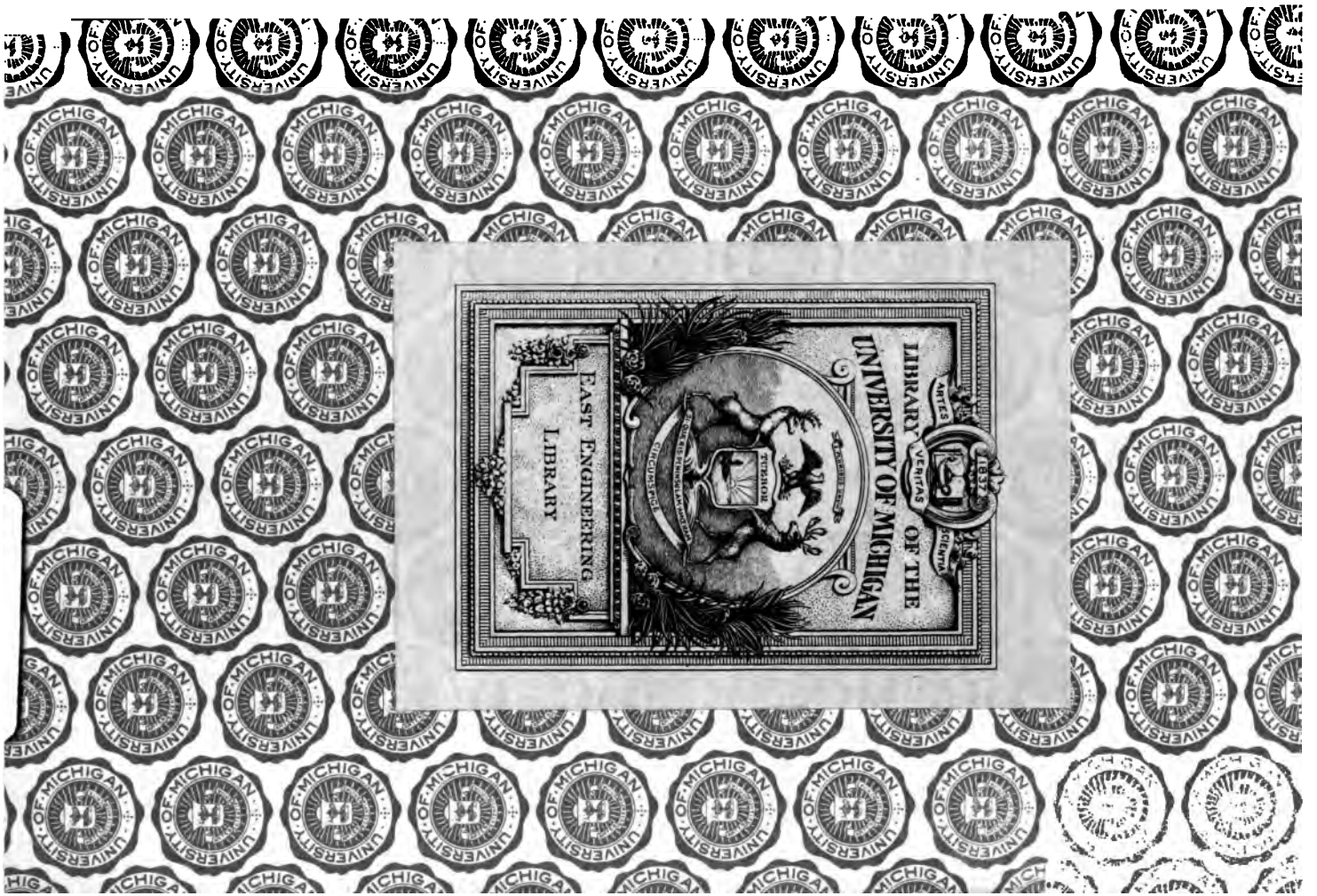
United States Steel Corporation

FOR THE

SAMPLING AND ANALYSIS

OF

PIG IRON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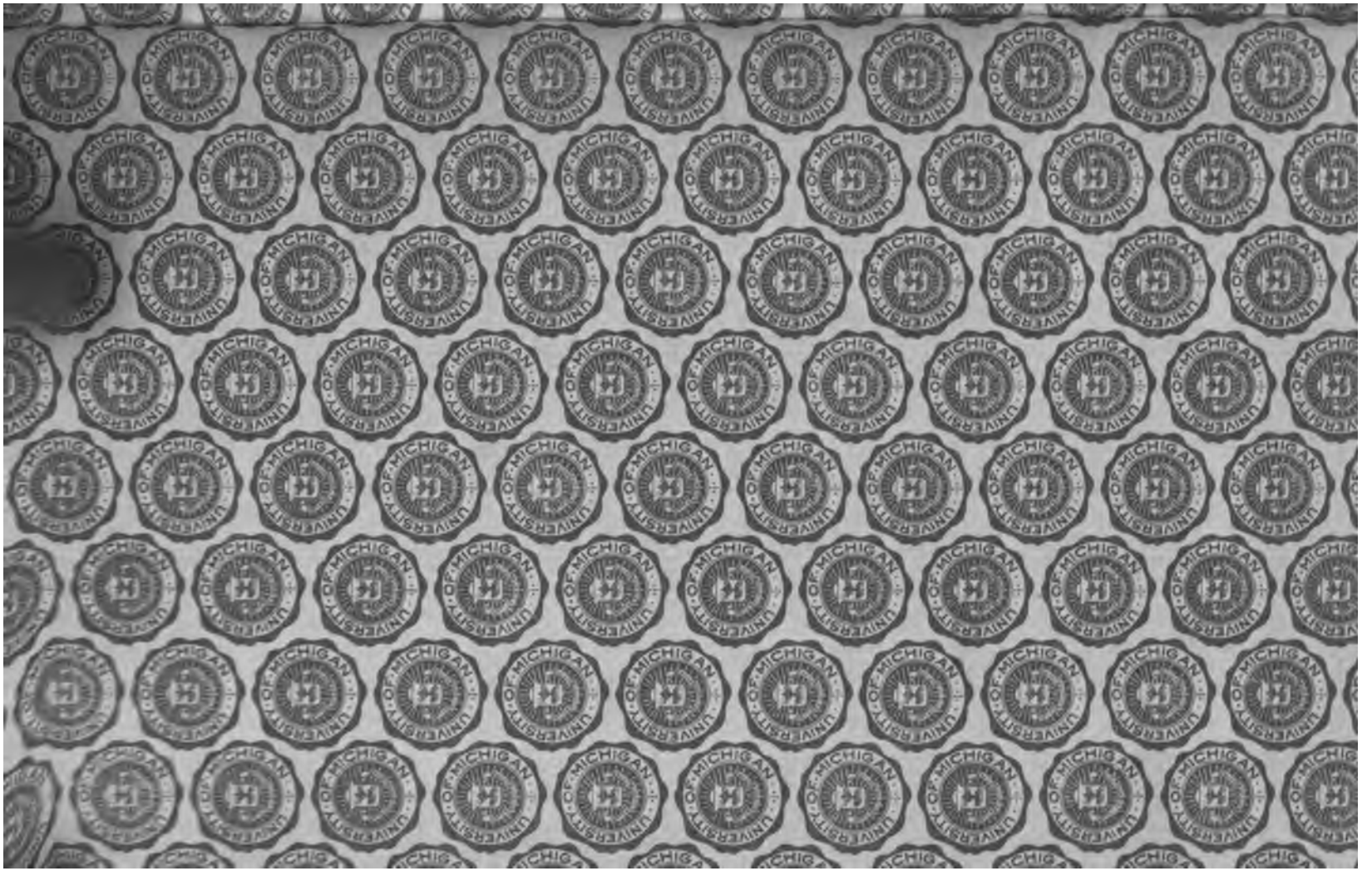
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METHODS

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United States Steel Corporation

FOR THE

SAMPLING AND ANALYSIS

OF

PIG IRON

PUBLISHED BY
CARNEGIE STEEL COMPANY
BUREAU OF INSTRUCTION
PITTSBURGH, PENNA.

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BY
J. M. CAMP
CHAIRMAN CHEMISTS' COMMITTEE
UNITED STATES STEEL CORPORATION

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PREFACE.

This pamphlet is intended to supersede one of a similar title, published by the Carnegie Steel Company, and first issued in 1912. Inasmuch as the methods for the sampling and analysis of pig iron have undergone considerable changes since the appearance of the former pamphlet, many of the methods as given therein may no longer be considered as representing good modern practice. A committee chosen from the chemists employed by the various subsidiary companies of the United States Steel Corporation was therefore appointed to revise and, if necessary, rewrite this pamphlet.

At its first meeting this committee decided that the pamphlet should be rewritten. In order to acquire complete knowledge of the latest practices, and for guidance in its work, the committee solicited the chemists of the various Works of the Corporation for recommendations concerning methods and operations that might be considered improvements over those appearing in the original edition. These recommendations have been given due consideration in the preparation of this pamphlet.

The committee of chemists under whose direction this pamphlet is produced is composed of the following persons: W. B. N. Hawk, Chief Chemist, Lorain Works, The National Tube Company; William Brady, Chief Chemist, South Works, Illinois Steel Company; and H. E. Campbell, Chief Chemist, Clairton Works, Carnegie Steel Company.

SAMPLING.

INTRODUCTORY REMARKS.

Rapid determination of the constituent elements of pig iron, with the exception of sulphur by the volumetric method, is susceptible of a very satisfactory degree of accuracy. With respect to sulphur the volumetric method is the only one, up to the present, by which the determination can be made within the time limits fixed upon the iron laboratory. The degree of accuracy attainable in a volumetric determination of sulphur, however, is largely dependent upon the grade of the iron and the condition under which the test is taken. A method of sampling molten iron which produces a highly chilled test, such as the water shot method, is not desirable, because such a condition in a test piece is conducive to low results when sulphur is determined thereon by the volumetric method. This is due to the fact that, upon dissolution of chilled iron in hydrochloric acid, volatile organic sulphur compounds are formed, which are lost in the process of volumetric determination on account of the inability of the absorbent solutions employed to retain them. The use of such chilled tests makes it necessary to anneal the sample previous to making the determination for sulphur, an operation that lengthens the time of and complicates the determination and is, therefore, to be avoided.

Inasmuch as the condition of chill is the predominant influence which causes the formation of non-absorbable gases, it is evident that a successful method for sampling molten iron should yield a test piece which is free from this objectionable condition. The method of casting in sand meets these requirements, and it has been found, moreover, that a sand cast sample gives an accurate measure of the sulphur content by the volumetric method. However, owing to the danger of contamination from the sand, this sand test is not suitable for the determination of silicon, nor has any method, practical for routine work, been devised for combining sand tests from different parts of a cast into one representative analytical sample.

The methods for sampling which are recommended herein, viz., the plate test method and the mould test method, do not give tests which are

entirely free from chill. However, the rate of cooling is not too rapid, evidently, to prevent certain transformations that take place on slow cooling, for it has been shown by a series of comparative tests by a number of chemists of the Corporation that there is a very satisfactory agreement in sulphur values as obtained by the evolution method on samples taken by these methods and by the sand cast method. Therefore, it has been decided to adopt these methods as standard procedure where molten iron is to be sampled.

SAMPLING OF MOLTEN METAL FROM THE BLAST FURNACE.

APPLIANCES FOR SAMPLING.

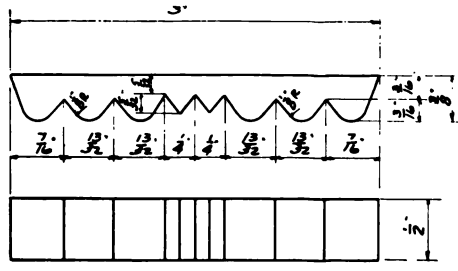
A spoon, or ladle, and either moulds or an iron plate are employed in taking samples of pig iron in the molten state. The spoon is similar to or the same as that employed about the furnaces regularly in taking fracture tests.

DESCRIPTION OF MOULDS AND PLATES.

Two forms of moulds are recommended, and the use of either is sanctioned. These moulds are made of cast iron, and are illustrated in detail, with dimensions, in figures 1 and 2. Both, it will be noted, are designed so that pieces of approximately the same size may be broken from different tests, thus making it convenient to combine individual tests into one representative sample of any body of molten metal.

The mould in figure 1 gives a test which may be conveniently broken into small pieces suitable for crushing. The number of the furnace may be cast in the mould with Roman numerals, or if the furnace is designated in another way, some other suitable symbol may be used. The two ridges shown in the test in this figure indicate that the test is taken from furnace No. 2.

The mould in figure No. 2 furnishes a test which may be either drilled or crushed. If the sample is to be crushed, the notched prolongation "T" is broken and crushed, and the main body of the test is reserved for the furnaceman's fracture test. The furnace number may be cast in this mould, but not so conveniently as the mould described above and only in the main body of the test.



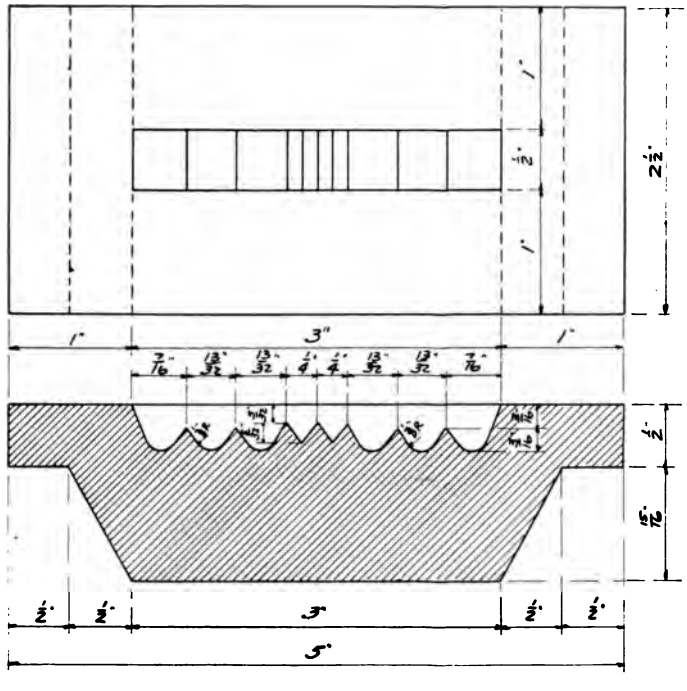
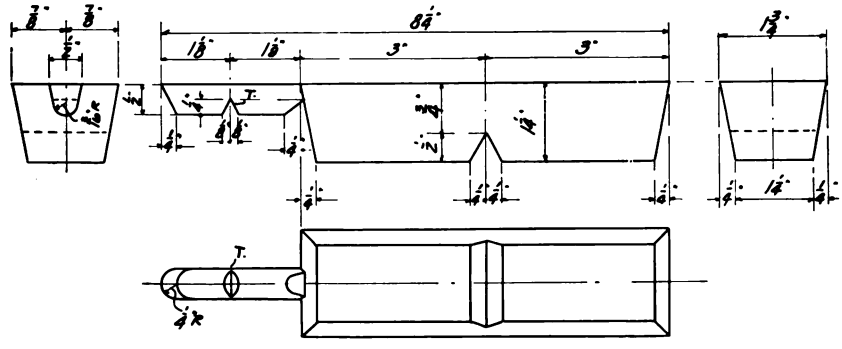


FIG. 1. TEST PIECE AND MOULD FOR SAMPLING MOLTEN PIG IRON FOR CHEMICAL ANALYSIS.



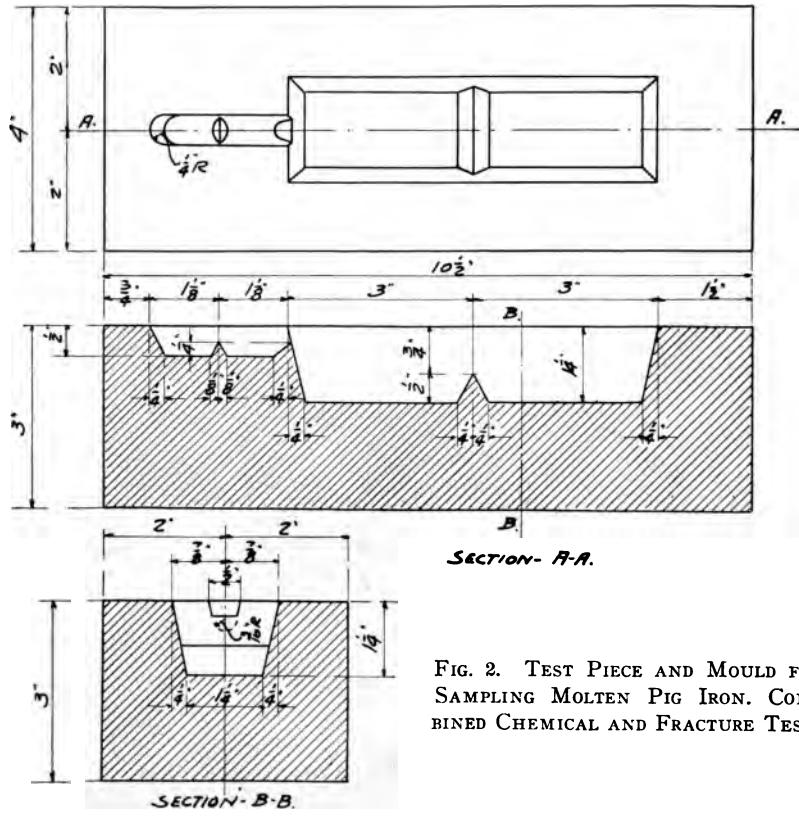


FIG. 2. TEST PIECE AND MOULD FOR SAMPLING MOLTEN PIG IRON. COMBINED CHEMICAL AND FRACTURE TEST.

Any iron or steel plate, which has a smooth surface and suitable dimensions, is satisfactory for use in the plate or pat test. As to size, the plate should provide a surface of at least one square foot and should not be less than eight inches in width.

ACCURACY AND CARE IN TAKING THE SAMPLE.

The ladle and mould or plate should be clean to insure an uncontaminated sample, and as a safety measure all the sampling appliances should be perfectly dried immediately before using.

Care should be taken to prevent the inclusion of slag or other foreign matter in the sample. This is accomplished as follows: Avoiding any material that may be floating on the surface of the metal, a full ladle of iron is dipped from the runner and part of it is immediately poured off, whereupon the test is poured by either of the following optional methods:

PLATE OR PAT TEST.

With the spoon resting on the plate, a pat approximately two inches in diameter or larger is poured thereon. Then changing the resting place of the spoon, another pat is poured, and these operations are repeated until all the molten metal in the spoon has thus been poured.

MOULD TEST.

With the spoon resting on the mould, sufficient metal is poured therein to fill the mould. Only one mouldful may be poured from each spoonful of the molten metal.

NUMBER OF SAMPLES TO BE TAKEN.

A representative sample is the basis of reliable chemical analysis. It is a well established fact that the first iron of a cast may vary greatly from the iron at the end of the cast. In order to obtain a representative sample, therefore, portions are taken from different parts of the cast, and equal quantities from each portion are combined in one lot. It is evident that each portion should represent the same proportion of the whole cast as any other portion. A convenient method is to secure a sample portion, timed as nearly as possible, from the middle of each ladle of iron in the cast.

PREPARATION OF THE SAMPLE.

The test pieces are either drilled or crushed as their size and form requires. In the case of pat tests the cleanest pat from each portion taken from the cast is selected, care being taken to have all these pats of approximately the same size. If desired, the pats are then broken with a hammer and a representative piece, or pieces, is selected from each and combined so that the sample for crushing will contain about the same amount of metal from each pat. In the case of the mould test the proper proportioning of the sample is much facilitated by the notches in the test piece, which make it easy to break off pieces of about the same size from the test pieces. When crushed, only that portion of the sample which passes through an eighty mesh sieve is used for analysis.

If the sample is to be prepared by drilling, a test piece cast in the test mould shown in figure 2, or one of similar form, is used, and the test piece is drilled to a suitable uniform depth from a cleaned area in its top and through its center. In this case sieving of the drillings is not permissible on account of the larger proportion of graphite present. Also the drill should be operated to give drillings as fine as practicable, else it will be very difficult to mix the drillings from the individual test pieces properly to form the sample for analysis.

SAMPLING FROM RAILROAD CAR AND STOCK PILE.

One pig is selected at random from each four tons of iron, and ten pigs, representing forty tons of iron, or an average car load, constitute a sample unit. This proportion will be found convenient for larger or smaller quantities of iron.

PREPARATION OF THE SAMPLE.

The surface of each pig is cleaned with a wire brush or by other suitable means to remove all loose sand. The skin is ground from the center of the top of each pig, exposing clean metal, by means of an emery wheel. Using a one-half inch twist drill, one hole is made in each pig, starting at the center of the cleaned space and stopping when the point of the drill appears below. To prevent loss of fine particles during drilling, a sheet metal disc is clamped to the cleaned surface of the pig. There should be a hole in the center of the disc large enough to admit the drill.

The drillings are either brushed off as they accumulate or after the drill is withdrawn. The pig is then inverted over a receptable to collect the drillings that remain in the hole.

The drillings from the entire unit are combined and weighed. They are then sieved, using 80 and 120 mesh sieves with covers. The portions remaining on each sieve and that passing through the 120 mesh are weighed separately and placed in glass-stoppered bottles which are appropriately labeled. Each portion is well mixed. A proportionate amount is taken from each bottle for the analysis sample, the exact weight of each depending upon the size of the sample desired.

Example.

The gross drillings of a certain sample weigh 500 grams and are separated into portions weighing 400 grams on the 80 mesh sieve, 80 grams on the 120 mesh sieve and 20 grams through the 120 mesh sieve. In this case, a 5 gram sample consists of 4 grams from the portion on the 80 mesh, .8 gram from the portion on the 120 mesh, and .2 gram from the portion through the 120 mesh.

METHODS OF ANALYSIS.

GENERAL CONSIDERATIONS.

A few statements in explanation of the use of reagents in these methods are deemed advisable.

Whenever water is mentioned it is understood to be distilled water. The concentration of the mineral acids and ammonia is indicated by the word concentrated, or by notation of the specific gravity, or by the proportion, by volume, of concentrated reagent to water in parenthesis. The word concentrated signifies that the ordinary chemically pure product as received from the manufacturer is used. Thus the specific gravities of concentrated sulphuric, nitric, and hydrochloric acids and ammonia are 1.84, 1.42, 1.19, and .90, respectively. In giving the proportion in parenthesis, the proportion of water is always given last. When per cent is employed to indicate the dilution of a reagent, the numeral expressing the per cent designates the number of grams of a solid, or cubic centimeters of a liquid, which is added to water to make 100 cc. of solution.

It is understood that all acid and chemicals mentioned are of chemically pure, or C. P., grade. Further, it is recommended that blank analysis be made of all reagents to determine their freedom from impurities that may affect the results of any of the analyses.

DETERMINATION OF SILICON.

DROWN'S METHOD.

A single or double factor weight, .4676 or .9351 gram, of the sample is transferred to a glazed porcelain dish, 15 to 25 cc. of the nitric-sulphuric acid mixture are added, gentle heat is applied to the covered dish, and the solution is evaporated to pronounced fumes of sulphuric anhydride. The dish is removed from the heat and allowed to cool. Fifty to sixty cubic centimeters of hydrochloric acid (1:10) are added, and the contents of the dish are heated without boiling until the soluble salts dissolve. The residue of silica and graphite is collected on a 9-cm. ashless filter and washed alternately with hydrochloric acid (1:10) and hot water to the disappearance of the soluble iron, and finally with hot water until free from chlorides. The residue and paper are transferred to a weighed crucible and ignited, uncovered, at a moderate temperature until the carbon is completely oxidized, and then for a few minutes at a higher temperature to dehydrate the silica. The residual weight is multiplied by 100 and adjusted in conformity with the initial weight of the sample to find the per cent silicon.

The silica obtained by this method may be slightly contaminated, and, when an occasion demands such a precaution, its purity is determined by volatilization with hydrofluoric acid. To do this, 2 drops of sulphuric acid (1:1) and 3 cc. hydrofluoric acid are added to the weighed residue. Gentle heat is applied until all fumes are evolved, when the crucible and residue are ignited at a high temperature and weighed. The loss in weight is silica. The per cent silicon is calculated as in the preceding paragraph.

SOLUTION REQUIRED.

Nitric-Sulphuric Acid Mixture.

Nitric acid (sp. gr. 1.20)	750 cc.
Sulphuric acid (1:1)	250 cc.

DETERMINATION OF SULPHUR.

VOLUMETRIC OR EVOLUTION METHOD.

The evolution method is not to be regarded as always yielding the exact sulphur content of the iron. This fact should be given due cognizance by all users of pig iron. However, it meets better than any other method the time requirements of the iron laboratory, and, when all conditions in connection with the sampling and analysis are properly controlled, it is sufficiently reliable to satisfy the demands of the various metallurgical processes in conjunction with which it is employed.

The apparatus recommended for this determination consists of a 300- to 500-cc. flask; a two-hole rubber stopper carrying an ordinary funnel or thistle tube and a glass exit tube bent at a right angle; a delivery tube, also bent at a right angle; and some suitable form of absorption vessel. The exit and delivery tubes are connected with sulphur-free rubber tubing, and the latter is inserted into the absorption vessel in such manner as to conduct the evolved gases to the bottom of the vessel. The absorption vessel may be either a tall form beaker of 500 to 600 cc. capacity, in which the titration is later conducted, or a test tube, preferably 10″ by 1″, suitably supported.

A minimum of 2.5 grams or a maximum of 5 grams of the sample is transferred to the flask, the stopper is inserted, and the flask is connected with the absorption vessel. Ten to twenty cubic centimeters of the absorbent solution are added to the absorption vessel and diluted to 60 cc. or 200 cc., depending upon whether a test tube or beaker is employed. Forty to sixty cubic centimeters of hydrochloric acid (1:1) are introduced into the flask through the funnel, and heat is applied so that a brisk evolution of the gases is maintained until the sample is decomposed. The temperature is then raised until the steam formed has forced the last trace of hydrogen sulphide gas into the absorbent, as indicated by a marked rise in temperature of the delivery tube above the point of entering the absorbent solution. The apparatus is disconnected and the titration is conducted as described below.

Ten cubic centimeters of starch solution are added to the beaker in which the titration is effected, and the contents of the absorption tube are transferred thereto. The absorption and delivery tubes are rinsed with cold water, which is added until the beaker contains at least 300 cc., when

any adhering precipitate is dissolved by means of a fine jet of hydrochloric acid (1:1). If the absorption is effected in the beaker, the delivery tube is removed and cleansed with acid and water. Then a slight excess of hydrochloric acid (1:1) is added. The final volume of the solution should approximate 400 cc. The solution is stirred gently in order to neutralize the alkali of the absorbent, but care is exercised that the liquid in the beaker be not unduly agitated before the introduction of the standard iodate solution. The standard iodate solution is then added in successive portions, while the solution is stirred as the color fades, until the addition of the final drop yields a permanent blue color of the adopted end point. The number of cubic centimeters of the standard iodate required multiplied by .01 is equivalent to per cent sulphur.

SOLUTIONS REQUIRED.

Standard Potassium Iodate Solution.

Potassium iodate	1.12	grams
Potassium iodide	12.	grams
Potassium hydroxide	1.	gram
Water to make	1000.	cc.

The iodate, iodide, and hydroxide are dissolved in 300 cc. of water. The solution is then diluted to 1000 cc. when it is ready for standardization. A standard steel, the sulphur content of which has been established gravimetrically, is used as a basis of standardization. With final adjustment so that 1 cc. is equivalent to .01 per cent sulphur, based upon the initial weight of the sample used, the solution is ready for use. It must be kept in the dark and in a cool place.

ABSORBENT SOLUTIONS.

Ammoniacal Cadmium Chloride Solution.

Cadmium chloride	5 grams
Water	375 cc.
Concentrated ammonia	625 cc.

Ammoniacal Zinc Sulphate Solution.

Zinc sulphate	10 grams.
Water	375 cc.
Concentrated ammonia	625 cc.

Sodium or Potassium Hydroxide Solution.

Sodium or potassium hydroxide	5 grams.
Water	1000 cc.

Starch Indicator Solution.

An emulsion of 6 grams of starch in 100 cc. of cold water is cautiously added to a liter of boiling water which is contained in a suitable flask. After continued boiling for five minutes, the contents of the flask are cooled, and 6 grams of zinc chloride in 50 cc. of cold water are added to preserve the solution. After thorough mixing, the flask is set aside for 24 hours with occasional shaking. When the heavier particles have settled, the supernatant liquid is carefully decanted into a suitable container.

It is recommended that the starch be added to boiling water, as this tends to lessen the often unavoidable frothing; should frothing occur, however, its subsidence may be effected by playing a jet of air over the surface of the boiling solution.

If desired, the starch indicator solution may be added to any of the stock absorbent solutions, thus affording the proper amount of indicator in the titrations without adding it separately in each case. The methods for mixing the starch solution with the different absorbent solutions are described in the paragraphs which follow.

Directions for Mixing Starch Indicator With Absorbents.

Starch indicator is incorporated into the stock solutions of cadmium chloride and zinc sulphate as follows: An emulsion of 6 grams of starch in 50 cc. of cold water is cautiously added to 250 cc. of boiling water which is contained in a suitable flask. After boiling for 5 minutes, the solution is set aside for 24 hours, when it is decanted from the residual particles. Five grams of cadmium chloride or 10 grams of zinc sulphate are dissolved in 75 cc. of water. Concentrated ammonia is then added until the precipitate, which at first forms, is dissolved. This solution is now combined with the starch solution, and the resultant solution is well mixed. Concentrated ammonia is added until the total volume is 1000 cc., when the solution is ready for use.

To combine starch indicator with sodium or potassium hydroxide, the procedure is as follows: An emulsion of 6 grams of starch in 50 cc. of water is slowly poured with stirring into a solution of 5 grams of sodium or potassium hydroxide in 50 cc. of water. When the starch is assimilated by the hydroxide, as indicated when the solution becomes almost clear, water is added to make a volume of 1000 cc. The solution is now ready for use.

GRAVIMETRIC METHODS.

I. SOLUTION OF SAMPLE IN NITRIC ACID.

Five grams of the sample are transferred to a beaker or an Erlenmeyer flask of at least 500 cc. capacity, and 100 cc. of concentrated nitric acid are added. The dissolution of the metal is accelerated by application of gentle heat, but care should be taken that the action does not become violent, else a loss of sulphur may result. The reaction may be retarded at any time by placing the beaker or flask in cold water.

The solution is evaporated to small volume and cooled, when 30 cc. of concentrated hydrochloric acid are added. The solution is again evaporated to small volume and transferred to a porcelain dish. One gram of sodium carbonate is added, the solution is then evaporated to complete dryness, and the residue is baked at a moderate temperature for 10 minutes. Forty cubic centimeters of concentrated hydrochloric acid are added to the dish, and a gentle heat is applied until the soluble portion dissolves. The contents of the dish are now evaporated to dryness and heated for 10 minutes at a temperature not to exceed 130° C. The residue is digested over a gentle heat with 60 cc. of hydrochloric acid (1:1) until soluble parts dissolve, whereupon 50 cc. of water are added and the solution is boiled for 5 minutes. The carbonaceous and siliceous material is collected on a filter and washed with hot hydrochloric acid (1:50) until the washings are free from iron solution. The dish containing the filtrate is placed on an asbestos pad, in order to prevent the formation of a crust of salts upon the sides of the dish, and the filtrate is evaporated in the open dish until the first appearance of a slight film of chlorides on the surface of the solution. The sulphur may now be precipitated by either of two methods.

1. WITHOUT PRELIMINARY REDUCTION OF THE IRON.

The film of chlorides is dissolved with a few drops of hydrochloric acid (1:1); 6 drops are usually sufficient. Cold water is added to a volume of 100 cc. Any insoluble residue is collected upon a filter paper, the filtrate being received in a 250 cc. beaker. The filter paper is washed with hot hydrochloric acid (1:50) and cold water, alternately, until the iron is completely removed, when the washing is conducted with hot water to a final volume of 200 cc. Ten cubic centimeters of a ten per cent solution of barium chloride are added to the cold solution, and, after standing for

24 hours with occasional stirring, the precipitated barium sulphate is ready for filtration. The supernatant liquid is decanted through a double 9 cm. filter paper. The precipitate is transferred to the paper by means of a jet of hydrochloric acid (1:50) and washed with the same until free from iron solution, then with hot water until free from chlorides. The filter and precipitate are ignited in a weighed uncovered platinum crucible at a moderate temperature until the carbon of the paper disappears and then at a slightly increased temperature for ten minutes. The weight of barium sulphate minus that found in the blank test is multiplied by 13.73 and the product is divided by the weight of the sample taken to obtain the per cent of sulphur.

Barium sulphate obtained in this manner is sometimes in a very finely divided state, and traces are often found in the filtrate and washings. This small amount can be recovered by filtration after the solution has been allowed to stand for 24 hours.

2. WITH PRELIMINARY REDUCTION OF THE IRON.

Five cubic centimeters of concentrated hydrochloric acid, 10 cc. of water, and 5 grams of 20 mesh, granulated, sulphur-free zinc are added to the solution. Heat is applied until the iron is reduced, more acid being added if necessary. The solution is filtered from the silica and the undissolved zinc, and diluted to 100 cc. Ten cubic centimeters of a ten per cent solution of barium chloride are added, and the solution is allowed to stand 18 to 24 hours. The barium sulphate is removed by filtration and the per cent sulphur is determined as detailed in 1.

The insoluble residue of carbonaceous and siliceous material should be examined for sulphur. The paper and residue are placed in a clean platinum crucible, covered with a layer of sodium carbonate, and ignited with a sulphur-free flame until the paper disappears. A little more sodium carbonate and a small amount of sodium nitrate are added, whereupon the residue is fused. The fusion is dissolved in hydrochloric acid (1:2), and the solution is evaporated to dryness. The silica is separated in the usual manner, and the filtrate is treated with barium chloride solution. Any precipitate, which forms after standing for a sufficient length of time, is collected on a filter together with any precipitate that may have separated in the original filtrate, and the combined weight is added to that already obtained.

A blank test to determine the amount of contamination from reagents should be made under the same conditions as described in the regular method. The weight of barium sulphate thus obtained is deducted from the gross weight found in the regular determination.

II. SOLUTION OF SAMPLE IN COPPER POTASSIUM CHLORIDE SOLUTION.

Five grams of the sample are transferred to a 400 cc. beaker and dissolved in 250 cc. of copper potassium chloride solution. The solution is filtered through an asbestos pad which is supported on a porcelain disc in a carbon filter tube, and the residue is washed two or three times with hydrochloric acid (1:20). The residue and asbestos pad are placed in the original beaker, and 20 cc. of concentrated nitric acid are added. Heat is applied, and crystals of sodium or potassium chlorate are introduced until the carbonaceous material is entirely decomposed. Five cubic centimeters of concentrated hydrochloric acid are then added to dissolve the precipitated manganese dioxide, whereupon the solution is filtered through an asbestos pad. The beaker and pad are washed with hot water. The solution is evaporated to dryness in a porcelain dish, ten cubic centimeters of concentrated hydrochloric acid are added, and the solution is again evaporated to dryness. The residue is digested with ten cubic centimeters of hydrochloric acid (1:50) and 20 cc. of water, whereupon the undissolved portion is removed by means of a 9 cm. filter.

The filtrate is heated to boiling, and 20 cc. of a ten per cent barium chloride solution are added. The solution is boiled gently for a short time, when the barium sulphate is separated by filtration. It is washed with hot water until free from chlorides, ignited slowly in an uncovered platinum crucible, and weighed. The weight of barium sulphate is multiplied by 13.73 and divided by 5 to obtain the percentage of sulphur.

The filtrate is allowed to stand for several hours. If any precipitate of barium sulphate separates, the amount is determined and added to the main precipitate.

A blank determination is made, and the result is applied as a correction to the regular determination.

SOLUTION REQUIRED.

Copper Potassium Chloride Solution.

Copper potassium chloride ($CuCl_2.2KCl$)	300 grams.
Concentrated hydrochloric acid	100 cc.
Water to make	1000 cc.

DETERMINATION OF PHOSPHORUS.

VOLUMETRIC METHOD.

One or two grams, depending upon whether the phosphorous content is above or below .15 per cent, of the sample are transferred to an Erlenmeyer flask of 250 cc. capacity, 40 to 50 cc. of nitric acid (sp. gr. 1.13) are added, and heat is applied until the sample is decomposed. Any material on the sides of the flask is washed into the solution by means of a jet of water, one gram of ammonium persulphate is added, and the solution is boiled until the combined carbon is completely oxidized. The solution is filtered, and the residue is washed with nitric acid (1:50) and hot water to the disappearance of the soluble iron. The filtrate is heated to boiling in a suitable flask, a slight excess of a solution of potassium permanganate is added, and the solution is boiled until the excess of permanganate is decomposed. A slight excess of a reducing solution is added to dissolve the precipitated manganese dioxide, and boiling is continued until the excess of the reducing agent is decomposed. The flask is removed from the heat, 50 cc. of ammonium molybdate solution are added, and the flask is shaken for five minutes. The yellow precipitate of ammonium phosphomolybdate, after settling, is collected upon a 9 cm. filter paper and washed with nitric acid (1:50) until free from iron solution and finally with a one per cent sodium nitrate solution until free from acid.

The titration may be conducted in either a 250 cc. beaker or the flask in which the precipitation was effected. If the former is used, care is exercised to remove any precipitate which adheres to the flask, while in the latter case, the flask is washed thoroughly with sodium nitrate solution to completely remove the acid.

The filter paper and precipitate are transferred to the beaker or flask, and a measured excess of standard sodium hydroxide solution is added. In case the titration is conducted in a beaker, the filter paper is macerated with a glass rod; if conducted in a flask, a clean rubber stopper is inserted, and the contents are shaken vigorously until the paper is disintegrated and the dissolution of the precipitate is complete. The solution is diluted to approximately 100 cc. with water free from carbon dioxide, and three drops of phenolphthalein solution are added, followed by standard nitric acid until the pink color disappears. The sides of the vessel are washed with

cold water, when the titration is completed by adding standard sodium hydroxide until the appearance of a permanent pink tint. The number of cubic centimeters of the standard sodium hydroxide solution in excess over the standard acid used, multiplied by .02 or .01, depending upon the initial weight of the sample taken, is the equivalent of phosphorus in hundredths per cent.

SOLUTIONS REQUIRED.

Standard Sodium Hydroxide Solution.

Sodium hydroxide	6.6	grams
Water	1000	cc.

Standard Nitric Acid.

Concentrated nitric acid	10	cc.
Water	990	cc.

The specified quantity of sodium hydroxide is dissolved in 500 cc. of water in a one liter graduated flask. One cubic centimeter of a saturated solution of barium hydroxide is added, when the solution is diluted to the mark and mixed thoroughly. After standing for 12 hours or more, a portion of the clear solution is removed with a pipette for standardizing. The acid and sodium hydroxide solutions are adjusted so that they exactly agree. They are then standardized by means of a steel of known phosphorus content and adjusted so that one cubic centimeter is equivalent to .01 per cent phosphorus based on an initial weight of two grams of the sample. The sodium hydroxide solution is now filtered through a dry filter into a suitable container and thereafter protected from the air as much as possible.

Phenolphthalein Indicator Solution.

Phenolphthalein	1	gram
Methyl or ethyl alcohol (neutral)	1000	cc.

Nitric Acid (Sp. Gr. 1.13).

Concentrated nitric acid	240	cc.
Water	760	cc.

Potassium Permanganate Solution.

Potassium permanganate	25	grams
Water	1000	cc.

Ammonium Molybdate Solution.

Molybdic acid (85 per cent)	65	grams
Water	142	cc.
Concentrated ammonia	143	cc.
Nitric acid (sp. gr. 1.20)	715	cc.

To the water in a suitable container is added the molybdic acid, followed by the ammonia. The contents of the vessel are shaken until the molybdic acid is dissolved, when the solution is cooled and poured slowly into the nitric acid, the latter being stirred constantly during the addition. To clarify the resultant solution, one drop of a ten per cent solution of ammonium phosphate is added. After agitation, the solution is allowed to stand for twelve hours when it is filtered, preferably by suction through an asbestos pad.

REDUCING SOLUTIONS.

Ammonium Bisulphite Solution.

Five per cent solution.

Ferrous Sulphate Solution.

Ferrous sulphate	50 grams
Sulphuric acid (1:1)	50 cc.
Water	950 cc.

Potassium Nitrite Solution.

Potassium nitrite	50 grams.
Water	1000 cc.

Sugar Solution.

Sugar	500 grams.
Water	1000 cc.

This sugar solution should be added carefully, a drop at a time, in order to avoid an excess over the amount necessary to reduce the manganese dioxide. Three or four drops should be sufficient.

RECOVERY OF MOLYBDIC ACID AND PREPARATION OF AMMONIUM MOLYBDATE SOLUTION FROM AMMONIUM PHOSPHOMOLYBDATE.

In methods when ammonium molybdate is employed as a precipitant, an economy may be effected by recovery of the molybdic acid from the filtrates. In case recovery is desired, washings from the operation of filtration are not permitted to mix with the filtrate proper, but the latter is transferred to a suitable container, for reservation, before washing of the precipitate is begun.

When a convenient quantity of the filtrate has been accumulated, it is heated to boiling, and a solution of commercial sodium phosphate is

added. The weight of sodium phosphate in this solution should be ten times the quantity of 85 per cent molybdic acid to be recovered, or 33 grams of sodium phosphate for the equivalent of each 50 cc. of ammonium molybdate solution treated. The solution is allowed to stand until the precipitate of phosphomolybdate has settled; it is then decanted and the precipitate is transferred to a wide mouth bottle of five liters capacity or larger. These operations are repeated until a sufficient quantity of the yellow precipitate has been collected, when it is washed by decantation with nitric acid (1:50). It is then transferred to a large dish, and the liquid is evaporated. When dry, this precipitate, or a mixture of this precipitate and molybdic acid, is employed for the preparation of ammonium molybdate solution. The recovered phosphomolybdate contains 92 per cent molybdic acid; hence, when used alone, 60 grams are sufficient to make one liter of the solution.

Ammonium molybdate solution is prepared from recovered phosphomolybdate as follows: Sixty grams of the phosphomolybdate are dissolved in 230 cc. of water and 170 cc. of ammonia. A solution of ten grams of commercial magnesium nitrate or sulphate dissolved in 30 cc. of water is now added to precipitate the phosphate. The flask is shaken, and the precipitate is allowed to settle, whereupon the solution is filtered, and the precipitate is washed with 30 cc. of ammonia (1:4). The filtrate is cautiously added to 540 cc. of nitric acid (1:1). The solution is now ready for use as needed.

GRAVIMETRIC METHOD.

WEIGHING AS AMMONIUM PHOSPHOMOLYBDATE.

For this determination from one to five grams of the sample are employed according to the phosphorus content. The weights recommended as most convenient are as follows: 5 grams in all cases where the probable phosphorus content is less than .100 per cent, 2.5 grams where it is between .100% and .200%, and 1 gram where it is above .200%.

The proper amount of the sample is weighed and transferred to a glazed porcelain dish, which is provided with a cover glass, and 25 to 60 cc. of nitric acid (sp. gr. 1.13) are cautiously added. Gentle heat is applied until the sample is decomposed, when the solution is evaporated rapidly to dryness. The cover glass is removed, and the dish and contents are heated with the full flame of an Argand or Bunsen burner until the acid

is completely expelled. After cooling, 30 to 40 cc. of concentrated hydrochloric acid are added, and gentle heat is applied until the soluble portion is dissolved. The dish is placed upon a suitable asbestos ring in order to prevent the formation of a crust of separated salts on the sides of the dish, and the solution is evaporated to the first appearance of a film upon its surface. The dish is then removed from the heat, 10 cc. of concentrated nitric acid are added, and heat is again applied for one minute. Approximately 40 cc. of cold water are added, when the solution is stirred and filtered through an 11 cm. filter paper into a 500 cc. flask. The filter is washed with cold nitric acid (1:50) until free from iron solution, which insures also the complete removal of the soluble phosphate.

In the case of very exact work, the residue of silica and graphitic carbon is examined for the presence of phosphorus as follows: The residue and filter paper are ignited in a platinum crucible, and the silica is volatilized with hydrofluoric acid in the presence of 2 or 3 drops of sulphuric acid. The resultant residue is mixed with a small amount of sodium carbonate, and the mixture is fused. The melt is disintegrated in hot water, the insoluble material is separated on a filter paper, and the filtrate, which contains the phosphate, is added to the main solution.

To the filtrate or filtrates are added 25 cc. of concentrated ammonia. The flask is shaken until the precipitate coagulates, when 25 cc. of concentrated nitric acid, which should be sufficient to dissolve the precipitate and allow an excess of 7 to 10 cc., are added. The comparatively large amounts of ammonia and nitric acid are prescribed in the case of five gram samples and are essential in that they insure a sufficient proportion of ammonium nitrate in the solution. When smaller quantities of the sample are used, the amount of ammonia may be decreased, but there should always be an excess of nitric acid as indicated.

The solution is heated to 80° C., 50 to 75 cc. of the molybdate solution are added, and the flask is shaken for five minutes. The yellow precipitate is allowed to settle, when it is collected upon a 9 cm. filter paper, which has been previously dried for one hour at a temperature of 115° C. and weighed between ground-edge watch glasses. The precipitate and paper are washed with nitric acid (1:50), dried in the same manner as the paper, and weighed.

The increase in weight, multiplied by 1.65 and divided by the initial weight of the sample taken, is equivalent to per cent phosphorus.

WEIGHING AS MAGNESIUM PYROPHOSPHATE.

The yellow precipitate of ammonium phosphomolybdate as obtained above, while still moist, is dissolved from the filter in a hot ammonium citrate solution, the filter is thoroughly washed with hot water, and the solution is retained in a 100 cc. beaker. Five to ten cubic centimeters of magnesia mixture are added to the cold solution, which is then stirred for five minutes. After standing for three hours, the precipitate of magnesium ammonium phosphate is collected upon a 9 cm. filter and washed with ammonia (1:4) until free from soluble salts. The precipitate and paper are transferred to a porcelain crucible and ignited at a low temperature for fifteen minutes and finally at a high temperature for ten minutes. The weight of magnesium pyrophosphate is multiplied by 27.87 and divided by the weight of the sample taken to find the percentage of phosphorus.

SOLUTIONS REQUIRED.

Ammonium Citrate Solution.

Citric acid	50 grams
Concentrated ammonia	350 cc.
Water	650 cc.

Magnesia Mixture.

Magnesium sulphate	84 grams
Ammonium chloride	250 grams
Water	665 cc.
Concentrated ammonia	335 cc.

DETERMINATION OF MANGANESE.

SODIUM BISMUTHATE METHOD.

One gram of the sample is transferred to a 250 cc. Erlenmeyer flask and dissolved in 50 cc. of nitric acid (sp. gr. 1.13). The solution is boiled to expel the nitrous oxide fumes, when it is cooled and filtered, the residue being washed with nitric acid (3:100). The filtrate is heated nearly to boiling, and the organic matter is oxidized by the addition of successive small quantities of sodium bismuthate until the pink color of permanganic acid persists or the brown oxide of manganese precipitates upon boiling. A three per cent solution of hydrogen peroxide or a five per cent solution of ammonium bisulphite is now added, a few drops at a time, until the manganese dioxide is dissolved. The excess of the reducing reagent is expelled by continued boiling. Ammonium persulphate may be substituted for bismuthate for oxidizing the organic matter; in this case, the excess ammonium persulphate is destroyed by boiling.

The solution is cooled rapidly to a temperature of about 15° C. and diluted to a volume of 50 cc. An excess of sodium bismuthate, from .5 to 1 gram, is added, whereupon the mixture is vigorously agitated. The solution is decanted through an asbestos filter, and the flask and filter are washed with nitric acid (3:100) until the washings are colorless. The nitric acid is freed from nitrous fumes immediately before dilution by bubbling air through it for twenty minutes or more. The solution is then transferred to a 250 cc. beaker and 3 cc. of phosphoric acid (sp. gr. 1.71) are added. Standard thirtieth normal ferrous ammonium sulphate solution is now added from a burette until an excess of approximately 10 cc. is obtained. The total volume used is noted. The excess ferrous ammonium sulphate is then determined by titration with standard thirtieth normal potassium permanganate solution. The difference between the volume of permanganate solution required and the volume of permanganate solution which is equivalent to the total volume of ferrous ammonium sulphate solution added is multiplied by the weight of manganese in one cubic centimeter of the standard permanganate solution. The result thus obtained is multiplied by 100 to find the percentage of manganese.

This method is susceptible of giving accurate results and is therefore recommended in cases where especial exactness is required. Care should

be exercised to exclude nitrous oxide fumes, organic matter, and chlorides from the solution to be titrated, for traces of these substances therein vitiate the results.

SOLUTIONS REQUIRED.

Sodium Oxalate Solution.

Sodium oxalate	1.000	gram
Water	1000	cc.

Thirtieth Normal Potassium Permanganate Solution.

Potassium permanganate	1.06	grams
Water	1000	cc.

The potassium salt is dissolved in boiling water, and the solution is allowed to stand for 24 hours. It is then filtered through an asbestos filter and standardized as follows: One hundred cubic centimeters of the sodium oxalate solution are transferred to a 400 cc. beaker, and 20 cc. of sulphuric acid (1:1) are added. The contents of the beaker are heated to 80° C., whereupon the standard permanganate is added, slowly at first and then rapidly, until a permanent pink tint is obtained. The weight of manganese equivalent to one cubic centimeter of the standard permanganate solution is found by the following calculation:

$$\frac{.0163958}{\text{(Volume in cubic centimeters of permanganate solution required to oxidize 100 cc. of the sodium oxalate solution.)}}$$

The figure .0163958 is the weight of manganese in the form of permanganate, expressed as the fraction of a gram, which is equivalent to 100 cc. (.1 gram sodium oxalate) of sodium oxalate solution.

Thirtieth Normal Ferrous Ammonium Sulphate Solution.

Ferrous ammonium sulphate	13.1	grams
Sulphuric acid (1:1)	100	cc.
Water to make	1000	cc.

Nitric Acid (Sp. Gr. 1.13).

Concentrated nitric acid	240	cc.
Water	760	cc.

PERSULPHATE-ARSENITE METHOD.

Five-hundredths to two-tenths gram of the sample is transferred to a 100 cc. flask, 15 cc. of nitric acid (sp. gr. 1.13) are added, and gentle heat is applied until the sample is decomposed. Five cubic centimeters of

a solution of ammonium persulphate are added, and the heating is continued until the combined carbon is completely oxidized. If graphitic carbon or silica separate in amount sufficient to render it necessary, the solution is filtered through a small filter paper, the filtrate being received in a flask similar to that previously used. The filter and residue are washed with the minimum of water or with 15 cc. of silver nitrate solution, which is required for the subsequent oxidation. The silver nitrate solution is introduced either through the filter or to the unfiltered solution, 10 cc. of ammonium persulphate solution are added, and heat is applied until the characteristic pink tint of the permanganic acid is well defined. The solution is then quickly cooled, when 10 cc. of sodium chloride solution are added to decompose the silver nitrate. After stirring, standard sodium arsenite solution is added until one drop just dispels the pink tint of permanganic acid. The addition of sodium chloride solution is unnecessary if the solution of permanganic acid is quite cold and the titration is conducted rapidly; otherwise, the excess of persulphate will react upon the reduced manganese with a resultant recurring end point. The number of cubic centimeters of the standard arsenite solution required multiplied by .1 gives the percentage of manganese in the sample.

If desired a greater initial weight of the sample may be taken, when the solution thereof is diluted to a definite volume, the graphite and silica are allowed to subside, and aliquot portions are withdrawn with a pipette.

SOLUTIONS REQUIRED.

Ammonium Persulphate Solution.

Ammonium persulphate	100 grams
Water	1000 cc.

Silver Nitrate Solution.

Silver nitrate	1.3 grams
Water	1000. cc.

If desired for convenience, the silver nitrate may be added to the nitric acid solvent in the proper proportion.

Sodium Chloride Solution.

Sodium chloride	2.5 grams
Water	1000. cc.

Standard Sodium Arsenite Solution.

Sodium arsenite	1.0 grams
Water	1000. cc.

The sodium arsenite solution is standardized by means of a standard steel or iron of known manganese content. It is adjusted, if necessary, so that one cubic centimeter is equivalent to one-tenth per cent manganese based upon the initial weight of the sample used.

Nitric Acid (Sp. Gr. 1.13).

Concentrated nitric acid	240 cc.
Water	760 cc.

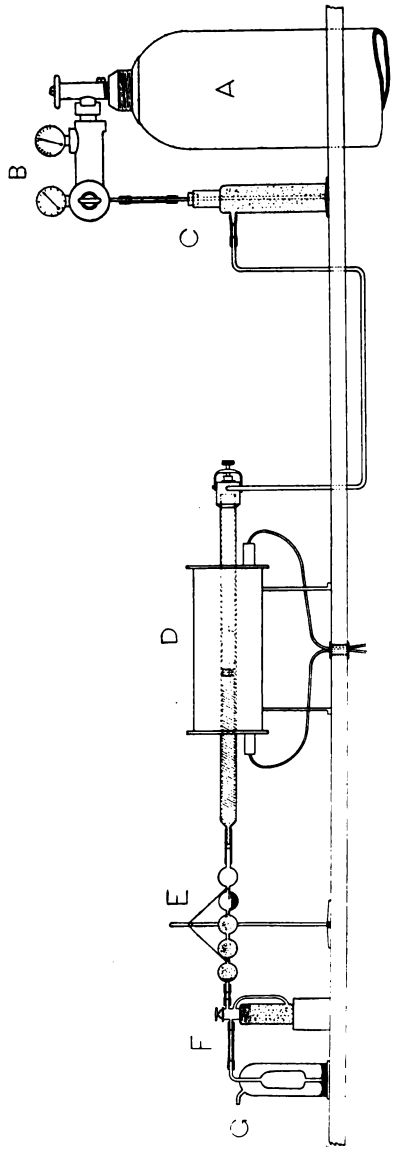


FIGURE 3. APPARATUS FOR THE DETERMINATION OF CARBON BY DIRECT COMBUSTION.

A. Oxygen tank. B. Pressure reducing and regulating valves. C. Purifying bottle. D. Combustion apparatus, showing packed silica tube in position in the electric furnace and proper location of the boat in same. E. Drying tube. This form is preferable, as it permits the viscous phosphoric acid to collect in the lower half of each bulb, as shown, without interferring with passage of the gases. F. Absorption bottle packed with soda lime or soda asbestos. G. Indicator bottle.

DETERMINATION OF TOTAL CARBON.

Carbon in pig iron is determined by direct combustion; that is, a portion of the sample in the form of powder or drillings is burned in a current of oxygen, and the resulting carbon dioxide is absorbed with soda lime or soda asbestos contained in a suitable bottle, and weighed.

The essential equipment for this determination is as follows: A combustion tube in which the sample of iron is burned; an electric furnace for heating the combustion tube; a rheostat for regulating the temperature, and possibly a transformer; a tank of compressed oxygen for burning the sample; a tube furnished with reagents for purifying the oxygen, if necessary; a boat to contain the sample during the combustion; a tube containing phosphorus pentoxide for drying the gases delivered from the combustion tube; an absorption bottle containing soda lime or soda asbestos for absorbing the carbon dioxide formed in burning the sample; an indicator bottle containing a solution of barium hydroxide; and proper connections for all these parts. This equipment with the exception of the rheostat and transformer is shown assembled for operation in the accompanying drawing of figure 3.

The electric furnace may be operated on either a direct or an alternating current. The latter, however, proves more satisfactory in that the high temperature required can be attained more readily, and the resistance wire does not burn out so quickly, provided the furnace is equipped with a transformer, which permits the voltage to be stepped down and the use of heavier resistance wire. The temperature of the furnace within the combustion zone must not be allowed to fall below 1000° C., and, in case of some samples of iron, a temperature of 1100° C., is necessary to obtain satisfactory results. For the exact regulation of the temperature, a pyrometer is necessary.

The combustion tube is made of fused silica, and is preferably of the form shown in the figure. It has a minimum inside diameter of 1 inch and a minimum length of 24 inches; the constricted portion at the exit end has a bore of ⅛ inch, an outside diameter of 5/16 inch, and a minimum length of 1 inch. The inlet end of the tube is preferably provided with a specially constructed brass stopper and gas inlet, as shown in figure 4. In this device, a nozzle, A, made to fit loosely over the end of the silica tube, S, is provided with a yoke, B, and set screw, C, which is employed

to clamp the cap, D, against the external gasket, E. A threaded hole shown at F is provided for a gas inlet. The stopper is firmly attached to the end of the silica tube by means of plaster of Paris, G, which is applied to the tube in the form of a thick paste just before it is inserted into the nozzle.

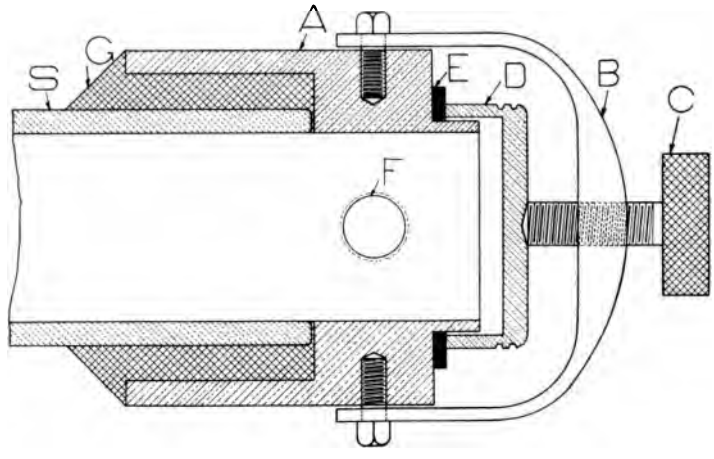


FIGURE 4. BRASS STOPPER AND GAS INLET FOR SILICA COMBUSTION TUBES USED IN THE DETERMINATION OF CARBON. FULL SIZE.

The end of the silica tube may be closed with a one-hole rubber stopper, and a piece of glass tubing used as a gas inlet, but in this case the stopper must be protected from the radiation of heat. To afford this protection a copper disc, or a plug of asbestos enclosed in nichrome gauze, is inserted into the tube with the stopper, and a water jacket should also be employed to keep the end of the tube cool. The tube is filled from the exit end to near the middle with asbestos impregnated with iron oxide. The impregnated asbestos is prepared by saturating shredded asbestos with a 10 per cent solution of ferrous sulphate, drying, and finally igniting at a temperature of 1000° C. The asbestos serves two purposes, viz., in the hot zone it acts as a catalyzer, oxidizing the carbon monoxide to carbon dioxide and the sulphur dioxide to sulphur trioxide, and, in the exit end of the tube, it prevents the radiation of heat. A sleeve, constructed of thin sheet nickel or nichrome and previously ignited at a temperature of 1000° C., may be inserted into the combustion zone to protect the walls of the tube from the iron oxide which has a tendency to splatter during the process of combustion.

The boat wherein the sample is burned is made of sheet nickel, sheet nichrome, clay, porcelain, or alundum. Of whatever material, it is protected from the sample by means of a layer of granular alundum or chrome ore, and, before using, the boat and lining material must be ignited for a length of time sufficient to free them from carbonaceous matter. The following dimensions for the boat will be found satisfactory: length, 3 to 3½ inches; depth, ¼ inch; width at bottom, ½ inch; and width at top, ⅝ inch. The high pressure cylinder which contains the oxygen is equipped with a pressure reducing valve and a stop-cock to regulate the flow of gas. A glass tower, lightly packed with soda asbestos or soda lime for extracting carbon dioxide from the oxygen, is placed in the line between the oxygen tank and combustion tube.

The apparatus which follow the combustion tube in order of position are the drying tube, the absorption bottle, and the indicator bottle. The drying tube is a suitable glass tube filled with phosphorus pentoxide. It is connected to the silica tube by means of rubber tubing. The container for the absorption of the carbon dioxide, known as the absorption bottle, is packed with soda asbestos or hydrated soda lime. When the latter is used, a layer of phosphorus pentoxide is placed in the top or exit end of the bottle for the purpose of recovering the moisture which is liberated from the soda lime during the absorption of carbon dioxide. The indicator bottle is an ordinary wash bottle partly filled with a two per cent solution of barium hydroxide and is connected to the exit end of the absorption bottle. The barium hydroxide solution serves to indicate the rate of flow of the gas through the apparatus and to give warning of any failure of the absorption bottle to retain the carbon dioxide produced by burning the sample.

In the determination, the oxygen is released from the pressure tank, and immediately passes through the purifying apparatus to assure its freedom from carbon dioxide. It then enters the combustion tube through the inlet appliance and encounters the boat containing the sample in the center of the hot zone. Here, partially or completely, the gas combines with the iron, while the portion which escapes, together with the generated carbon dioxide and sulphur dioxide, is forced through the asbestos packing. The sulphur compound is converted to sulphur trioxide and retained by the asbestos, and the other gases pass through the drying tube to the absorption vessel, where the carbon dioxide is collected by the proper reagent.

The sulphur trioxide which collects in the asbestos packing, as noted in the preceding paragraph, should be expelled occasionally lest the asbestos become saturated and allow it to pass into the absorption apparatus. To do this, a moderate flow of oxygen is started through the apparatus, the rubber connection is removed from the exit end of the combustion tube, and the tube is moved backward until the exit half is within the hot furnace. Sulphur trioxide, if present, will appear as white fumes issuing from the end of the tube. The operation is continued until the fumes are no longer emitted, when the displaced parts are restored to their normal position.

The apparatus being assembled and all connections made, the outfit is ready for a blank test. To make this, the procedure is as follows: The stop-cock of the absorption bottle is opened, and oxygen is admitted to the apparatus at such a rate that a continuous bubbling is observed in the indicator bottle. After ten minutes, the oxygen is discontinued, the stop-cock of the absorption bottle is closed, and the bottle is weighed, using a similar bottle as counterpoise. The bottle is now placed in position, and gas is again passed through the train for ten minutes, when the absorption bottle is reweighed. If the weight is the same as before, the blank is zero, which indicates that the gas and apparatus are free of carbonaceous impurities. The apparatus is now ready for a determination. This may be conducted either by the rapid oxidation method or by the slow oxidation method at the option of the operator.

RAPID OXIDATION METHOD.

A V-shaped depression or furrow about 2½ inches in length is made in the refractory material contained in the combustion boat, and a multiple of the factor weight (.2728 gram), preferably a 5-multiple (1.364 grams), of the sample is transferred thereto. In case of iron samples that are difficult to fuse, a portion of powdered cupric oxide or finely divided steel of low and known carbon content is mixed with the sample to assist in the oxidation. The cupric oxide should be ignited before using. When steel is employed, a correction must be applied for the carbon contained therein. The stop-cock of the absorption bottle is now opened. The metal cap or rubber stopper and plug are removed from the entrance end of the combustion tube, and the boat containing the sample is quickly placed in the center of the combustion zone. The metal cap or plug and stopper are instantly replaced and secured, when oxygen is admitted at such a rate that a continuous bubbling is observed in the indicator bottle.

In the course of one or two minutes, the sample will begin to oxidize, and the rate of bubbling in the indicator bottle will decrease. When the sample is completely oxidized, a sudden acceleration of the bubbling will occur. At this point, the rate of flow of the oxygen may either be maintained at the original rate or slightly reduced, and is so maintained for a period of from five to ten minutes. The current of oxygen is discontinued, and the absorption bottle is disconnected and weighed. The increase in weight of the bottle, expressed as the fraction of a gram, is divided by the multiplier of the factor weight used and multiplied by 100. The result is the percentage of total carbon in the sample.

SLOW OXIDATION METHOD.

This method differs from the preceding one only in the rate and length of time by which the oxygen is admitted to the combustion tube. In this method the flow of oxygen is regulated so that three bubbles per second escape through the indicator bottle, and this rate of flow is maintained for 30 minutes.

Fusion of the sample is seldom effected by this method. The particles of iron generally retain their original shape yet they are completely oxidized.

DETERMINATION OF GRAPHITIC CARBON.

An appropriate multiple of the factor weight (.2728 gram) of the sample is transferred to a 250 cc. beaker. Forty cubic centimeters of nitric acid (sp. gr. 1.13) are added, and a gentle heat is applied until the sample is decomposed. A few drops of hydrofluoric acid are introduced to the solution for the purpose of eliminating the silicic acid which, otherwise, has a tendency to clog the filter in a subsequent operation. The solution is then boiled for a few minutes, when the residue is collected on an asbestos pad. This pad is held in a perforated platinum or nickel boat, a Gooch crucible, or other suitable form of apparatus. The residue is washed alternately with hot hydrochloric acid (1:1) and cold water until free from iron, and finally with hot water until free from acid.

The graphitic residue and pad are now partially dried, whereupon they are ignited in a combustion apparatus, and the measure of graphitic carbon is established as in the case of total carbon in the preceding method.

The weight of carbon dioxide absorbed is divided by the multiplier of the factor weight used and multiplied by 100 to find the percentage of graphitic carbon in the sample.

DETERMINATION OF COMBINED CARBON.

The percentage of combined carbon is found indirectly by subtracting the percentage value of graphitic carbon from the value of total carbon as determined by the preceding methods.

DETERMINATION OF TITANIUM.

Five grams of the sample are placed in a 600 cc. beaker and digested in 100 cc. of hydrochloric acid (1:1) until all dissolving action has ceased. Ammonia is added until a flocculent precipitate is formed; the solution, however, should still react acid to litmus paper. Three cubic centimeters of concentrated hydrochloric acid are introduced, and water is added to make a volume of 300 cc. Fifty cubic centimeters of a 20 per cent solution of sodium thiosulphate are added, whereupon the solution is boiled for ten minutes. The insoluble matter is collected on a filter paper, washed with hot water, and ignited carefully in a porcelain crucible. The residue is transferred to a platinum crucible, and ten drops of sulphuric acid (1:1) and 5 cc. of hydrofluoric acid are added. Heat is now gently applied to the crucible to volatilize the silica and evolve the excess of sulphuric acid. The crucible and contents are finally ignited in a muffle furnace for 10 or 15 minutes to expel all traces of hydrofluoric acid. The residue is fused with a small amount of sodium carbonate, and the fusion is dissolved in sulphuric acid (1:4). The titanium is now in condition to be measured by colorimetric comparison as detailed in the following paragraph.

The sulphuric acid solution of the titanium or an aliquot portion thereof, if necessary, is transferred to a stoppered 250 cc. color comparison tube, 5 cc. of hydrogen peroxide solution are added, and the two solutions are thoroughly mixed, when the whole is diluted to a volume that will give a depth of color suitable for comparison. Into a similar tube are placed 5 cc. of hydrogen peroxide, which is followed by a five per cent solution of sulphuric acid until the volume of the mixture is enough smaller than that of the unknown solution to permit the addition of the standard solution to follow. Standard titanium sulphate solution is now added from a burette in successive portions until, after thorough mixing, the color matches that of the unknown solution, when it is diluted to the same volume, again thoroughly mixed, and its color compared with the unknown solution. The determination is completed by carefully matching the colors after the addition, if necessary, of one or more drops of the standard solution. The number of cubic centimeters of the standard solution used indicates the amount of titanium present.

SOLUTIONS REQUIRED.

Standard Titanium Sulphate Solution.

One and five-hundredths grams of ignited titanic acid are fused with 10 grams of sodium carbonate; the fusion is disintegrated in 100 cc. of water in a 400 cc. beaker, and the crucible and lid are placed therein. One hundred cubic centimeters of sulphuric acid (1:4) are added, and heat is applied until all particles are dissolved. The solution is transferred to a 1000 cc. volumetric flask and diluted to the mark with water. One cubic centimeter of this solution should equal approximately .0006 gram of titanium. The exact amount of titanium is found and the solution thus standardized by procedure as follows: Fifty cubic centimeters of the solution are transferred to a beaker by means of a pipette: ammonia is added until the solution is nearly neutral, and the titanium is precipitated with sodium thiosulphate solution as described on the preceding page. The titanic acid thus obtained is collected on a filter paper, washed, ignited, and weighed. The weight of titania is multiplied by the factor .6005 and divided by 50. The result is the value of titanium in one cubic centimeter of the standard solution.

Hydrogen Peroxide Solution.

Sodium peroxide	7 grams
Sulphuric acid (1:1)	250 cc.
Water	750 cc.

The water and acid are mixed, and the sodium peroxide is added to the mixture in successive small portions. After each addition, the solution is cooled to room temperature.

DETERMINATION OF COPPER.

Five grams of the sample are transferred to a glazed porcelain dish, and 40 cc. of nitric acid (sp. gr. 1.20) and 25 cc. sulphuric acid (1:1) are added. A cover glass is placed on the dish, and heat is applied until fumes of sulphuric anhydride are copiously evolved. Ten cubic centimeters of sulphuric acid (1:1) are added, followed by 50 cc. of hot water, when the dish and contents are heated until the salts are dissolved. The insoluble material is collected on a filter and washed thoroughly with hot water, the filtrate being received in a 600 cc. beaker. The filtrate is diluted to a volume of 300 cc. and heated to boiling. Fifty to seventy cubic centimeters of a 50 per cent solution of sodium thiosulphate are then added, whereupon the boiling is continued for 5 minutes or until the precipitate of copper sulphide has coagulated. The precipitate is collected upon an 11 cm. filter paper and washed with a two per cent solution of sulphuric acid and hot water. The quantity of copper may be determined gravimetrically or volumetrically as described later.

If preferred, and there is no occasion to speed the analysis, the sample may be dissolved in sulphuric acid instead of nitric acid and sulphuric acid. In this case, 5 grams of the sample are transferred to a 600 cc. beaker, 150 cc. of sulphuric acid (1:5) are added, and heat is applied until the sample is decomposed. The insoluble material is removed by filtration, and the filtrate is diluted, if necessary, to a volume of 300 cc., when the copper is precipitated with 30 cc. of a 20 per cent sodium thiosulphate solution. The determination is concluded as described above.

GRAVIMETRIC METHOD.

The filter and the precipitate of copper sulphide are ignited at a low temperature, and the resultant copper oxide is weighed. Since copper oxide is somewhat hygroscopic, care should be exercised that the residue in the crucible does not absorb moisture from the air.

The ignited copper oxide is contaminated with traces of iron and possibly titanium. It is dissolved in the crucible with 10 cc. of concentrated nitric acid, and the solution is transferred to a 250 cc. beaker and diluted to 100 cc. The iron is precipitated with ammonia, and the precipitate is collected upon a filter paper, washed with hot water, and ignited in the crucible in which the previous ignition was made. The weight is now taken,

and it is deducted from the weight of the crucible and impure copper oxide; the difference is pure copper oxide. The per cent of copper is calculated by multiplying the weight of pure copper oxide by the factor 79.89 and dividing the product by the weight of the sample used.

VOLUMETRIC METHOD.

The nitric acid solution of the impure copper oxide, which is obtained as explained in the gravimetric method, is transferred to a 250 cc. beaker and rapidly evaporated to the smallest volume possible in order to remove the greater portion of the free acid. The solution is then diluted with cold water to a volume of 150 cc. Ammonia is added from a burette until the addition of a drop develops a permanent blue color in the solution, whereupon 6 drops of acetic acid are introduced by means of a pipette. Ten cubic centimeters of a 40 per cent solution of potassium iodide are added, and, after stirring the solution, standard sodium thiosulphate solution is added until the color of the liberated iodine has almost disappeared. Ten cubic centimeters of the starch solution are now added, and the addition of the standard sodium thiosulphate solution is continued to the final disappearance of the blue color. The number of cubic centimeters of the sodium thiosulphate solution required is multiplied by its value in terms of copper, and the product is divided by the weight of the sample used. The result thus obtained is the per cent of copper in the sample.

The apparently large excess of potassium iodide is employed because of its relation to the end point in the titration, the sharpness of which decreases in proportion as the excess of iodide is decreased. The presence of ammonium salt in the solution tends to lessen the permanency of the end point; hence, the necessity for the preliminary evaporation of the acid solution.

SOLUTIONS REQUIRED.

Standard Sodium Thiosulphate Solution.

Sodium thiosulphate	8 grams
Water	1000 cc.

One cubic centimeter of this solution is equal to approximately .002 gram copper. The exact amount may be determined and the solution thus standardized by titrating as described above the nitric acid solution of approximately .05 gram of pure copper, accurately weighed.

Starch Indicator Solution.

Directions for preparing this solution are given on page 16 under the determination of sulphur.